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Hydrogen role in the valorization of integrated steelworks process off-gases through methane and methanol syntheses☆

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Abstract. The valorization of integrated steelworks process off-gases as feedstock for synthesizing methane and methanol is in line with European Green Deal challenges. However, this target can be generally achieved only through process off-gases enrichment with hydrogen and use of cutting-edge syntheses reactors coupled to advanced control systems. These aspects are addressed in the RFCS project i^{3}upgrade and the central role of hydrogen was evident from the first stages of the project. First stationary scenario analyses showed that the required hydrogen amount is significant and existing renewable hydrogen production technologies are not ready to satisfy the demand in an economic perspective. The poor availability of low-cost green hydrogen as one of the main barriers for producing methane and methanol from process off-gases is further highlighted in the application of an ad-hoc developed dispatch controller for managing hydrogen intensified syntheses in integrated steelworks. The dispatch controller considers both economic and environmental impacts in the cost function and, although significant environmental benefits are obtainable by exploiting process off-gases in the syntheses, the current hydrogen costs highly affect the dispatch controller decisions. This underlines the need for big scale green hydrogen production processes and dedicated green markets for hydrogen-intensive industries, which would ensure easy access to this fundamental gas paving the way for a C-lean and more sustainable steel production.

Keywords: process-off gases valorization / green hydrogen use / methane and methanol syntheses / advanced control / steelmaking industry sustainability

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1 Introduction

The European Green Deal represents the new plan of the European Union (EU) for sustainable growth. It aims at achieving the following main targets in EU [1]:
– European climate neutrality by 2050;
– protection of human life, animals and plants by the reduction of pollution;
– leadership for clean products and technologies;
– inclusive transition.

Several actions are required in the different sectors of the European economy (i.e., energy, buildings, industry, mobility) to reach the previous listed objectives. In the industrial field, two important actions are expected: the complete implementation of circular economy approach and the decarbonization, especially of Energy Intensive Industries. In particular, the decarbonization would lead to significant reduction of Greenhouse Gases (GHG) emissions with consequent contribution to mitigation of climate changes.

In this context, the steel sector is still one of the most impacting from the point of view of CO_2 emissions, despite important and continuous improvements. The steelmaking GHG emissions correspond to about 6% of the total EU emissions with an amount of 221 Mt GHG per year through direct and indirect emissions [2]. Valorization of current Process Off-Gases (POGs) would be a good option to reduce CO_2 emissions of steelmaking industries in the transition period required for a full adaptation/conversion of current processes in C-lean ones (e.g., direct reduction by hydrogen). A possibility of POGs valorization focused on the production of methane and methanol is addressed in the present paper by highlighting the fundamental role of hydrogen to achieve the proposed objective.

Considering the integrated steel route, three valuable POGs are produced in the main production steps: Coke Oven Gas (COG), generated by cokemaking, Blast Furnace Gas (BFG), arising from pig iron production, and Basic Oxygen Furnace Gas (BOFG), which is discontinuously generated during the conversion of pig iron into steel. The main features and standard uses of these POGs are provided in the infographic reported in Figure 1. The POGs main compounds are CO_x (in different ratios) and H_2, therefore they have a good Net Calorific Value (NCV) and are used especially for internal heat and energy production. Generally, before their use, they are stored in dedicated gasholders but a not optimized distribution as well as not synchronized production steps can lead to the following two situations:
1. gas surplus, when gas must be flared in torches with consequent avoidable and useless GHG emissions (valuable resources are burned and waste without giving any energetic advantage);
2. gas lack, when Natural Gas (NG) must be purchased.

For these reasons, in the last years some research activities were focused on optimization of POGs internal use to avoid the mentioned situations. Optimization is achieved through offline distribution analyses [3,4] and network layout optimization [5] as well as development of online decision support tools [6]. However, POGs similarity to syngas makes them suitable also for production of chemicals, such as methane and methanol, to be sold outside the steelworks or, in the case of methane, also to be used internally in place of fresh NG.

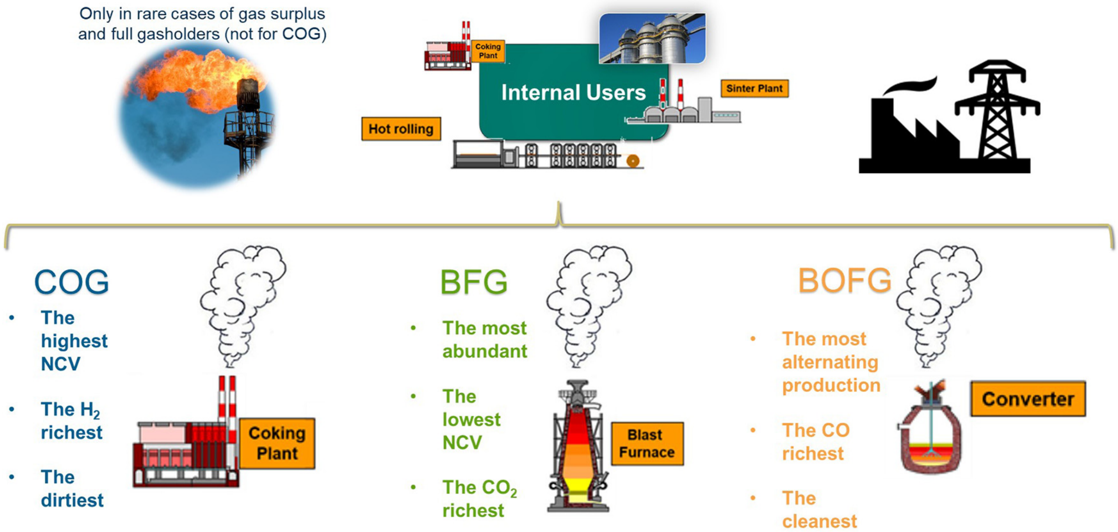
Methane production from steelworks POGs was preliminary investigated in [7]. On the other side, methanol production was already analyzed in the 1980s [8,9] but at that time the technology was not mature enough to attract further investigations. In the last years, methanol production from CO_2 rich gases (e.g., steelworks POGs) became again of interest of scientific community [10–12].

Both the valorization solutions (energy and material-based) can be jointly considered for maximizing POGs exploitation, recovering resources and possibly mitigating CO_2 emissions. In case of POGs material-based valorization, addressed in the paper, understanding the reason of CO_2 emission reduction could be counterintuitive. The understanding is simple if obtained products are used as intermediate for the productions of other chemicals but it is more difficult in the case of their heating or energy exploitation. However, firstly, the transformation of surplus POGs, otherwise flared in torches, leads to a complete avoidance of related emission of CO_2. In addition, if, for instance, methane produced with the use of green H_2 enriched POGs is exploited for internal heating or energetic purposes, CO_2 emission is reduced for two further reasons:
– CO_2 related to the extraction, preparation and transportation of primary NG to be otherwise bought is avoided;
– less gas is burned for the same amount of internally produced energy because methane holds a significantly higher NCV than POGs and less CO_2 is released by the combustion (see Sect. 5 and Tab. 4).

However, the following elements are needed, for the production of methane and methanol from POGs:
– hydrogen enrichment of gases as anticipated in the previous paragraph;
– cutting edge syntheses reactors;
– a Dispatch Controller (DC) to properly manage the enrichment and dispatching of POGs between reactors by considering gas-availability, internal standard uses (i.e., energy-based exploitations), operating costs and environmental advantages.

In particular, the first point underlines a further application that hydrogen can have in the steelmaking industry besides its use for direct reduction and/or as fuel. Nevertheless, most literature works on hydrogen application in steelmaking industry are focused on technological aspects and barriers to direct reduction [13–16]. Fewer investigations can be found on the use of hydrogen for heating purposes [17,18] and, based on our knowledge, no one related to the hydrogen role for the valorization of POGs.

The present paper highlights the importance of sustainable and green hydrogen production as enabler for Integrated Steelworks POGs (IS-POGs) valorization through methane and methanol production. In particular, after a brief introduction of hydrogen intensified methane and methanol syntheses from IS-POGs, provided in Section 2, and a description of the used models and controller, given in Section 3, Section 4 provides the



Compound	Vol. %
N_2	2.9
CO_2	1.2
CO	5.8
H_2	65.7
CH_4	21.8
C_nH_m	2.5
O_2	0.1

Compound	Vol. %
N_2	48.3
CO_2	23.1
CO	24.9
H_2	3.7
CH_4	traces
C_nH_m	traces
O_2	traces

Compound	Vol. %
N_2	27.6
CO_2	20.0
CO	51.8
H_2	0.6
CH_4	-
C_nH_m	-
O_2	traces

Fig. 1. Infographic about main features of integrated steelworks POGs and standard uses.

summary of some preliminary stationary simulation analyses. These investigations, already treated in detail by the authors in [19,20], are here reported to give initial estimations of required hydrogen and information about sustainable hydrogen production routes. Starting from these assumptions, a DC application for managing the POGs enrichment and distribution between methane syntheses reactors, internal users and Power Plant (PP) is investigated in details. These last analyses, treated in the Section 5, show how hydrogen costs represent one of the main barriers in the short medium-term for this POGs. valorization route. Finally, Section 6 provides some concluding remarks and hints for the future.

2 Hydrogen intensified methane and methanol syntheses from IS-POGS

The main reactions involved in methane synthesis are the following [21]:

$$CO + 3H_2 \rightarrow CH_4 + H_2O, \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \quad (2)$$

while the ones involved in methanol formation are listed below [22]:

$$CO + 2H_2 \rightarrow CH_3OH, \quad (3)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O. \quad (4)$$

In both the cases, the previous listed hydrogenation reactions can be combined together to obtain the reverse water gas shift reaction (5); that indicates a dependency in-between the reaction systems.

$$CO_2 + H_2 \rightarrow CO + H_2O. \quad (5)$$

Both reactions require the use of a catalysts and suitable ratios between the reagents to allow a high products yield. The variables expressing these ratios are the Stoichiometric Numbers (SN) reported in the following equations, respectively, for methane (6) and methanol (7) syntheses.

$$SN_{CH_4} = \frac{[H_2]}{3[CO] + 4[CO_2]} \in [1 \quad 1.1], \quad (6)$$

$$SN_{CH_3OH} = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \in [1.5 \quad 2.1]. \quad (7)$$

Equation (7) is less intuitive than (6); it is a rearrangement of the following more intuitive stoichiometric ratio (R_{CH3OH}) for syngas:

$$R_{CH_3OH} = \frac{[H_2]}{2[CO] + 3[CO_2]}. \quad (8)$$

Table 1. Requirements for the production of 1 kg of hydrogen from three different renewable-based processes [19].

		PEM	SOEC	Biomass Gasification
H_2O feed	kg/kg_{H2}	10	9	–
Required energy	kWh/kg_{H2}	55	42	–
Thermodynamic electrolyzer efficiency	%	63	84	–
Biomass feed	kg/kg_{H2}	–	–	8
Biomass gasification efficiency	%	–	–	13
CO_2 produced	kg/kg_{H2}	0[a]	0[a]	7

[a] if green energy is exploited.

When R_{CH3OH} is 1, the syngas is balanced or stoichiometric. However, for the methanol synthesis, SN_{CH3OH} is more exploited than R_{CH3OH}. If equation (3) occurred alone, the molar stoichiometric number H_2/CO would be 2; but reaction (5) consumes 1 mol of H_2 and produces 1 mol of CO per mole of existing CO_2, thus H_2/CO should be corrected as in (7). However, considering that SN_{CH3OH} needs to be 2 to get a balanced or stoichiometric syngas, and rearranging it, R_{CH3OH} is obtained.

Although IS-POGs are potentially suitable for these syntheses, their compositions do not satisfy the SNs, and their further features (e.g., the amount of minor contaminants) and availability affects their exploitation for the syntheses.

Among POGs, BFG and BOFG are the richest, respectively, in CO_2 and CO, but their H_2 amount is not sufficient for reaching the required SNs. In addition, BFG is the most abundant but least suitable POG for internal heating and energetic uses, while BOFG is produced in a discontinuous way due to the nature of converter process. On the other hand, COG, that is continuously produced, has the highest H_2 content, but it is the POG with the highest amount of minor contaminants. Thus COG is mostly suitable for heating and energetic purposes and mostly unsuitable for syntheses reactions, as, without a highly efficient cleaning treatment process, some of its components (e.g., H_2S, NH_3), if not removed, would poison the reactors catalysts. Therefore, in the dynamic scenarios of this study, only BFG and BOFG are considered as possible feedstock for the synthesis reactors after their enrichment with hydrogen and with the possibility of their mixing, while COG is considered only for internal usages. This does not mean that COG is a priori unsuitable. Actually, it is a good hydrogen feedstock for enriching the gas mixture, but it requires additional cleaning processes that increase both capital and operative costs of the process. The optimization of the COG cleaning processes is out of the scope of the present work, although it is an interesting topic for future research.

Finally, to avoid negative environmental impacts connected to hydrogen production, only hydrogen production processes from renewable are taken into account.

3 Materials and methods

Different models were developed for addressing two main tasks:

– preliminary investigations for comparing hydrogen production processes from renewable and for having a first estimate of hydrogen requirements in case of different end-products amounts;

– control applications for offline dynamic scenarios investigations as well as for online control of the POGs dispatching and enrichment (the online application is not described in the present paper).

In the first case, stationary flowsheeting-based models were developed, while in the second case a different methodology for modelling the processes dynamics was exploited (e.g., black box models exploiting Machine Learning (ML) techniques, accurate mathematical-based models and linear ones) and implemented within an ad-hoc settled DC.

3.1 Stationary models for preliminary investigations

Stationary flowsheeting models for preliminary investigations were developed by exploiting the commercial software Aspen Plus®. They include different operation units for simulating a complete chain involving hydrogen production, integrated steelworks POGs conditioning, methane and methanol syntheses. In particular, three different hydrogen production processes from renewable were modeled: a polymer electrolyte membrane (PEM) electrolysis, a solid oxide electrolyzer cell (SOEC) electrolysis and a biomass gasification. In the case of electrolizers, only use of green energy was considered. Literature data and producer's information were both used for modelling, tuning and validation steps.

The main results in terms of requirements for the production of 1 kg of hydrogen in standard operating conditions [19] are reported in Table 1; they are in accordance with reference data used for model validation.

Regarding POGs conditioning, furthers POGs treatments to be added to the standard ones were proposed and modelled to remove all undesired minor contaminants that can poison the reactors catalysts. In particular, the following treatments steps were considered: particle filtration, halogen removal (e.g., HCl through Nachcolite following the reaction (9)), Sulphur containing compounds elimination through the cascade use of a hydrodesulfurization reactor (e.g., according to the reactions (10) and (11)) and an adsorption technology based on the exploitation of ZnO bed as solid sorbent (as for instance in reaction (12)), further impurities removal by a guard bed containing nickel and a final drying stage.

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2, \tag{9}$$

$$COS + H_2 \rightarrow H_2S + CO, \tag{10}$$

$$CS_2 + 4H_2 \rightarrow 2H_2S + CH_4, \tag{11}$$

$$H_2S + ZnO \rightarrow H_2O + ZnS. \tag{12}$$

The methane and methanol syntheses were modelled by including reactions (1)–(5) and exploiting an approach based on the thermodynamic model using the Gibbs free energy minimization. In both models, simulation results showed a deviation $< 5\%$ from reference conditions used for models validation.

The detailed description of models development is out of the scope of the present paper, being hydrogen production models and all the other models described, respectively, in [19] and [20].

3.2 Models for control applications

In the present application, for dynamic scenarios and control purposes, the dynamics of involved processes need be reproduced, and the pursued approach aims at balancing models accuracy and computational cost to effectively include them in the control strategy. Controlling synthesis reactors in the context of integrated steelworks means having a clear vision of the dynamics of the plant as a whole, being production of methane and methanol linked not only to economic feasibility, but also to actual availability of sufficient POGs in gasholders. As already explained in the introduction, POGs are typically used internally to produce electricity and for other internal applications and such demands need to be satisfied.

A large set of models were developed for the control application aimed at:

– forecasting the POGs production and consumption based on production planning;
– describing the synthesis reactor dynamics in terms of products volume flow based on gas mixture at the inlet;
– describing and forecasting the dynamics of the main users and equipment, such as gasholders, PP and hydrogen production system;
– forecasting the trends of energy and emission media market prices related to electricity, NG, products and CO_2.

3.2.1 POGs production forecasting

The core of POGs' distribution optimization system is a set of models aimed at predicting their production over time based on the scheduling of the main processes (BF, BOF and Coke Ovens). Starting from the experience gained during the EU-funded project GASNET [6,23–25], the selected modelling strategy is based on a particular ML approach named Echo State Neural Networks (ESN) [26] that allows forecasting POGs production in terms of volume flow and gas components (e.g., CO, CO_2, H_2, O_2, N_2, CH_4 contents), by using as inputs the production plan and the continuously monitored variables that mostly affect the targets. The accuracy of models depends on the prediction horizon, which, in this application, is set to maximum 2 h ahead. The performance of the models is assessed through the Normal Root Mean Square Error (NRMSE) as defined in equation (13):

$$NRMSE = 100 \cdot \frac{\sqrt{\frac{1}{T} \cdot \sum_{t=1}^{T} (p(t) - h(t))^2}}{\max(h) - \min(h)}, \tag{13}$$

here p and h are, respectively, the predicted and historic values, t is the time along the timeseries, and T is the number of samples.

In the case of volume flow forecasting, validation NRMSE lays in a range between 1–11%, while for the composition lies in a range between 1–19% (Tab. 2), which is sufficient for control purposes.

The highest error values correspond to processes having a complex dynamics and to the prediction of the farthest values on the forecasting horizon. An example of prediction is reported for BFG and BOFG volume flowrate and CO_2 content in Figure 2.

Table 2. Performances of POGs production models.

Model	Outputs	NRMSE [%]
COG	Volume flowrate	1.7–4.8
	CO_2	2.4–2.7
	CO	3.3–4.7
	H_2	1.7–4.6
BFG	Volume flowrate	0.1–1.6
	CO_2	0.8–5.2
	CO	0.6–3.2
	H_2	0.4–3.6
BOFG	Volume flowrate	7.5–10.5
	CO_2	0.8–10.8
	CO	1.1–5.7
	O_2	0.9–19.2

3.2.2 Syntheses reactors

Three different innovative synthesis reactors were erected that, respectively, focus on the production of methane (two different reactors concepts with different synthesis behaviour) [27–33] and methanol [34,35] from hydrogen enriched IS-POGs. They were exploited for extensive experimental campaigns to study their behaviour and optimize their operating parameters. Both stationary and dynamic tests were carried out by varying volume flows, gas mixtures, H_2

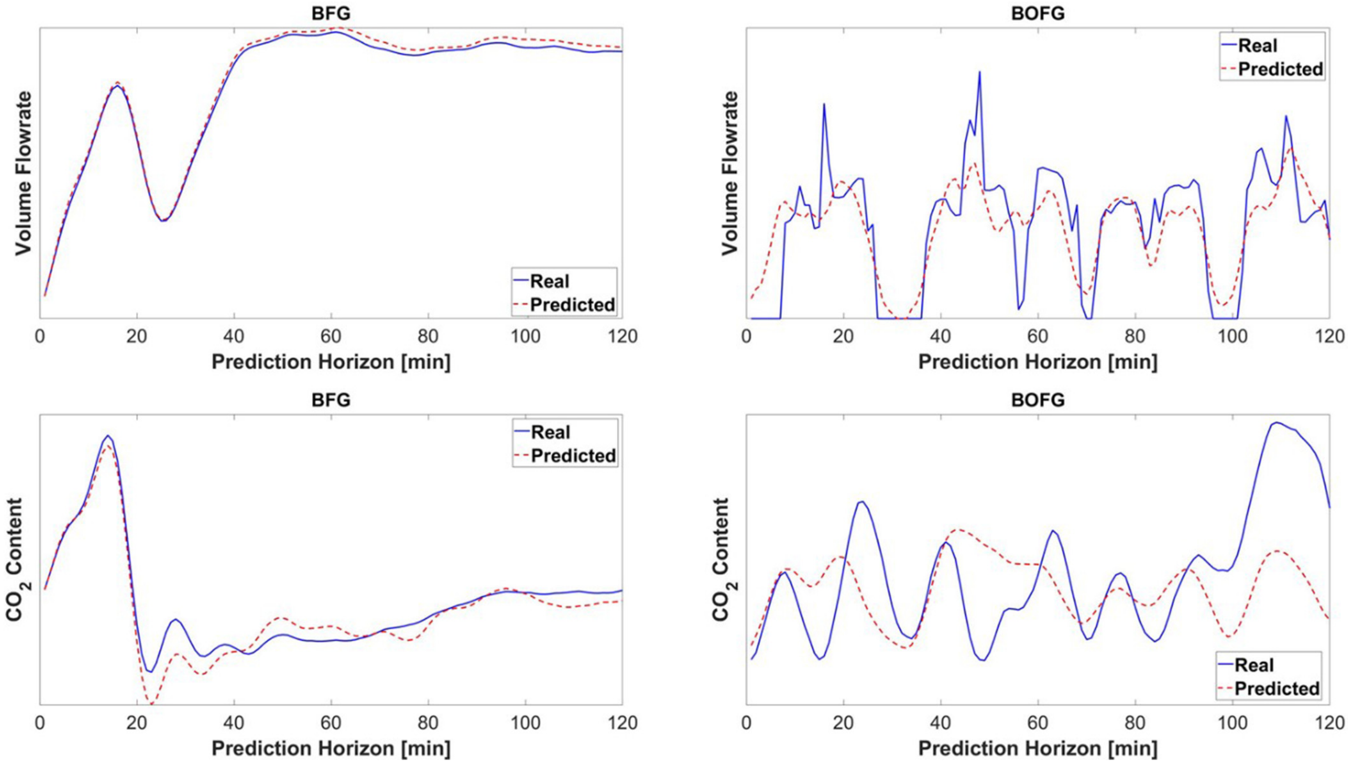


Fig. 2. Prediction examples of POGs forecasting models (y-axes values are not reported for confidentiality reasons).

amount, SNs and further operating parameters such as pressure, temperature and recirculation. CO_x conversions, products yield, temperature profiles as well as catalyst deactivation were monitored and the obtained results are promising. In particular, for methane reactors, full CO_x conversion was obtained in steady-state experiments and only small variations in the case of dynamic tests (CO_x conversion is always higher than 98%); in addition, high methane yield was achieved [27,28,31]. On the other side for methanol reactors CO_x and H_2 conversions vary respectively between 61–88% and 63–82%; in addition, the by-products formation, the temperature profile and peak temperature are in the common range expected for the new reactor concept [35].

Accurate models were then developed for describing the products volume flow in function of the gas mixture at their inlet. The models, developed within MATLAB/Simulink® environment, integrate chemical and physical equations, whose parameters were tuned and validated through real data resulting from the extensive measurement and experimentation campaign tests. The resulting nonlinear models are an important part of the DC that will be described in Section 3.3.

3.2.3 POGs users and equipment

The main POGs route within integrated steelworks is their exploitation for heating purposes and in PP for producing electricity and steam. In this specific application, the PP must share the POGs excess with synthesis reactors and, to optimize their distribution, it is fundamental to describe its efficiency as a function of the requested operative point. To this aim, the PP was described by a linear static model, with the objective of capturing the transformation efficiency of the thermal energy of gas mixture at the inlet of the electric PP.

Other main internal POGs users, such as hot blast stoves, hot rolling mills, etc., were modelled by taking into account their mean consumption considering a reference real integrated steel factory. The corresponding standard POGs distribution among the different users in the reference plant is depicted in Figure 3 (also PP is included in the figure). The figure shows also a common practice that is mixing POGs (sometimes also with NG) to obtain a mixed enriched gas characterized by a higher calorific value, which is generally used in PP.

An important component of the set of models describes the hydrogen production system. For the control application it was assumed to use a commercial system currently available in the market, whose dynamics are particularly fast. Therefore, a linear static model is sufficient to compute hydrogen production as a function of electric power consumption of a PEM electrolyzer (its choice depends on the preliminary stationary investigations, see Sect. 4), whose parameters are computed from related datasheets of commercial units.

3.2.4 Energy and emission media market

The feasibility of methane and methanol production starting from hydrogen-enriched POGs strictly depends on the prices of energy media and of CO_2 emissions that are ruled by the market. Their fluctuation can be characterized by variations every 15 minutes in the case

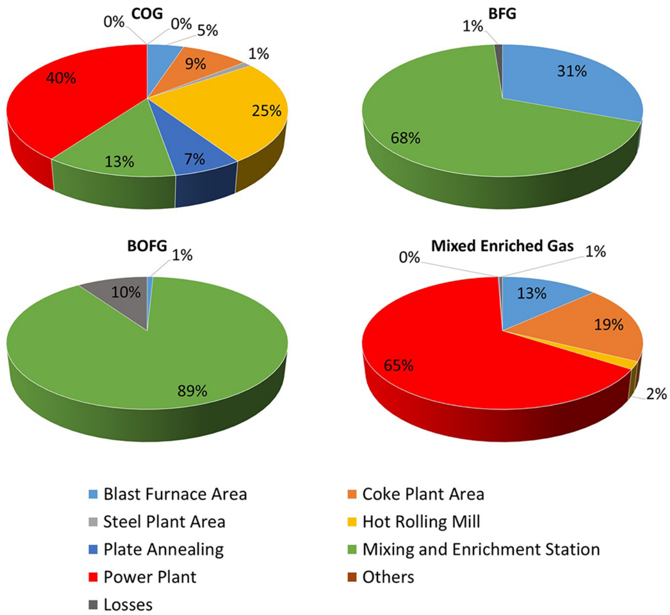


Fig. 3. Standard distribution of POGs in the considered reference plant.

of electricity, or on a daily basis for NG and CO_2. Therefore, price forecasting is fundamental for optimal POGs distribution.

Energy and emissions average prices are forecasted starting from their past trends through ML and, in particular, Feed Forward Neural Networks (FFNN). The accuracy of the models is in line with the status-quo of the energy and emission media price literature predictions [36–40]. Lower performances were obtained for the electricity price prediction. The main reason is the higher volatility of electricity prices with respect to NG and CO_2 ones.

3.3 Process off-gas dispatch controller

In general, within integrated steelworks, the exploitation of POGs as energy carriers requires an intelligent and optimized distribution to cover the needs of the internal users while also guaranteeing a sufficient electrical energy production in PP. Typically, optimal distribution aims at both generating economic gains and minimizing environmental impact, by minimizing flaring. Exploiting POGs for methanation and methanol production introduces the additional task of optimizing the hydrogen production for enriching POGs to reach the required SNs (see Sect. 2) and start reaction syntheses ensuring the economic feasibility. Optimal control of POGs distribution also requires that the involved gas networks, processes and equipment safely operate with a regime lying within their operating limits. To achieve these objectives, the DC must operate at both high and low level, supervising the operations of the whole plant, and jointly calculating in real-time appropriate loading strategies for each component. The architecture of the methane and methanol production system is shown in Figure 4, which depicts the data and control communication flows among plants and DC, the internal hydrogen and methane routes, and the POGs distribution to users and equipment.

More in detail, the DC implements an Economic Hybrid Model Predictive Controller (EHMPC) [41,42] that minimizes economic and environmental costs of POGs distribution. The cost function is formulated as follows:

$$\mathrm{J(x(k),u(k))} = \sum_{\mathrm{k=ci}}^{\mathrm{ci+N_p}} (\mathrm{C_{PEM}(k) + C_T(k) + Opex(k)} \\ \mathrm{+ C_{CO_2}(k) - C_{ES}(k) - C_{MEOH}(k) - C_{CH_4}(k)}), \quad (14)$$

where ci is the current control instant, N_P is the prediction horizon, and the other terms are the contributions to the cost functions related, respectively, to the green electric power consumption in the PEM electrolyzer (C_{PEM}), the waste of POGs excess in the torches (C_T), the operative costs of the plant ($Opex$), CO_2 emissions (C_{CO2}), and to the revenues linked with the internal production of electricity (C_{ES}), methanol and methane sold to external users (C_{MEOH} and C_{CH4}).

The strength of the EHMPC strategy lies in the ability to ensure real-time satisfaction of all plants operating constraints and optimality of a cost function (which can describe energy consumption, economic and environmental costs, etc.), thanks to the capability to forecast with good approximation the future behaviour of all involved plants. This feature is guaranteed by a large set of models (see Sect. 3.2) that are included in the control strategy. The system to control is highly nonlinear due to the synthesis reactors. In this specific application, to solve the optimization problem in real-time, the EHMPC implements a Mixed Integer Linear Problem, which describes the operation and limits of the plant through a linearization of the non-linear models at any instant, with a control frequency of 1 minute and a prediction and control horizon of 2 h.

The control application was developed in MATLAB environment, through optimization routines based on YALMIP [43] and GUROBI [44].

4 Preliminary stationary investigations

Preliminary investigations were carried out by using the stationary flowsheeting models described in Section 3.1. They aim at two main purposes:

- exploring the advantages and limitations of the different considered hydrogen production processes by varying operating parameters, and selecting the most suitable process to be applied in the hydrogen intensified methane and methanol production from IS-POGs;
- preliminary estimating hydrogen requirements and related required electric power in scenarios characterized by different amount of methane and methanol production and, consequently, by a different POGs exploitation in synthesis reactors.

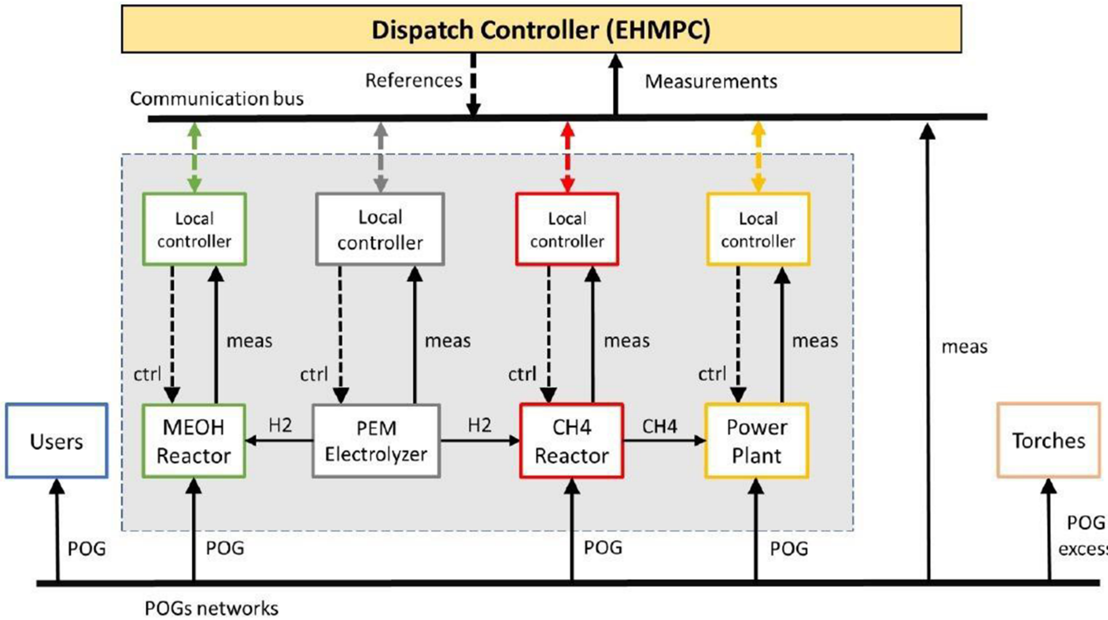


Fig. 4. Architecture of the methanol and methane production system.

The detailed descriptions of these investigations are provided in [19,20]. The main results are here reported to introduce the dynamic scenario investigations.

From the point of view of hydrogen production, the following main considerations were obtained after ad-hoc simulations for the three considered production options [19]:

– Biomass Gasification, although exploiting a renewable source (i.e., biomass), leads to the production of a syngas with high content of hydrogen but with a significant content of CO_2 (see Tab. 1) that increases by increasing the steam/biomass ratio and by decreasing the gasifier temperature as reported in Table 3.

In addition, due to the complexity of the plants, it appears less suitable to the integration in steelworks (especially considering the potential H_2 requirements).

– SOEC electrolyzer provides highly pure hydrogen with higher water and energy efficiency with respect to the other considered electrolyzer (see Tab. 1). It is convenient especially if a high-temperature heat source is available but the high-involved temperatures imply higher equipment costs and corrosion issues. An important aspect to prevent oxidizing environment by pure steam at high temperature is the partial recirculation of hydrogen in the cathode inlet but, as analyzed in [19], its increase leads to an increase of required power and a decrease of the efficiency of the process; therefore, a trade-off must be reached.

– PEM electrolyzer provides highly pure hydrogen as well, with slightly lower water and energy efficiency with respect to SOEC electrolyzer (see Tab. 1), but does not show issues related to high temperatures; moreover, it is more stable in case of power supply fluctuations typical of green energy. An important parameter for the process is the cathode pressure, as analyzed in [19]: its increase from 12 to 30 bar decreases required power of about 1.5% and water consumption of about 5.5%. However, undesired products permeation between the sections of cathode and anode is favored by the increase of cathode pressure, and management becomes more complex. A compromise is needed.

Table 3. Effect of steam/biomass ratio and of gasifier temperature on H_2 and CO_2 content in produced syngas [19].

Steam/biomass ratio	**H_2**	**CO_2**
	mol%	**mol%**
0.2	55.4	30.9
0.4	56.6	28.9
0.6	59.1	24.8
0.8	60.6	21.8
1	61.7	19.4

Temperature	**H_2**	**CO_2**
°C	**mol%**	**mol%**
700	61.7	18.5
750	61.5	17.3
800	61.2	16.4
850	60.8	15.5
900	60.5	14.8
950	60.2	14.1

Fig. 5. Explored stationary scenarios.

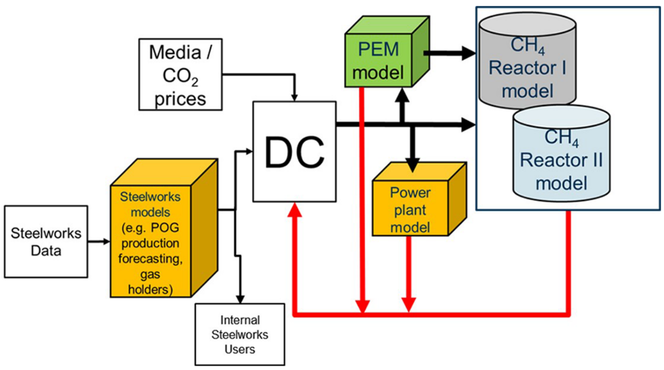


Fig. 6. Simplified control architecture referred to the carried out scenario investigations.

The previous considerations led to the selection of the PEM technology, fed by green energy, as mostly suitable for integration in steelworks. Therefore, the further studies were carried out considering only this hydrogen production technology.

The stationary scenarios explored with the complete hydrogen intensified methane and methanol production chain model [20], are summarized in Figure 5. The analyses consider a steelmaking plant of medium size with an annual steel production of about 6 MT.

The most realistic scenario is the third one. However, in all cases the required amount of hydrogen varies from 0.07 to 0.11 kg/kg_{POGs} and, consequently, the energetic requirement for electrolyzers is of the order of magnitude of the GW_{el} (i.e., from about 0.7 GW_{el} to 3.2 GW_{el}). Significant advantages in terms of energy and cost savings can be obtained from residual hydrogen recirculation: for instance, a recirculation of 75% of residual hydrogen could lead to a decrease of PEM energetic requirements respectively of about 50% (for the fourth scenario in Fig. 5) and of about 25% (for the fifth scenario in Fig. 5). Anyhow the current capacities of available hydrogen production technologies (also of PEM ones) are not yet suitable for satisfying the requirements for applying the explored scenarios in an integrated steelworks.

These preliminary investigations were the bases for deeper investigations carried out by simulating real states and related dynamics and applying the developed DC for an optimal POGs exploitation both in energetic and material-based way.

5 Dynamic scenario analyses

Offline dynamic scenario analyses were carried out to simulate as realistically as possible the integration of syntheses reactors in an integrated steelworks by considering the variation of production planning and consequently POGs availability.

Historical data from a real integrated steelworks were used to this aim. The renewable energy prices, which are highly linked to hydrogen production, were varied in the different simulations between 5 to 50 €/MWh (this last corresponds to about the current green energy prices) to underline the role of hydrogen production in the POGs dispatching.

All simulations were executed by assuming the same time horizon to consider the same production and internal consumption of POGs and to facilitate the result comparison. The scenario investigations were performed by considering only two of the three reactors: methanol synthesis was not considered at this stage. For the two methane synthesis reactors, a start-up time of 100 minutes for warming the reactors is considered and a SN of 1.04 was fixed for both the reactors. In addition, as anticipated in Section 2, only BFG and BOFG were used as feedstock for the synthesis reactors, while COG was exploited only for internal users and for the production of electric energy in PP. Two main usage options were considered for the produced methane: exploitation in PP and external sale. A simplified control architecture with respect to the one reported in Figure 4, adapted for the considered scenarios, is depicted in Figure 6.

As expected, the most affecting variables for POGs use in syntheses reactors are the filling level of the gasometers and especially the hydrogen production costs (directly linked with green energy prices). This can be easily observed in Figure 7 and Figure 8, concerning simulations of almost 13 h carried out, respectively, using a green energy price of 5 €/MWh (Scenario 1) and 18 €/MWh (Scenario 2). In the figures, COG is not reported because it does not affect the methane production.

In both figures "a" the POGs produced volume flowrate (light blue) and their consumption by internal users (orange) are shown. The almost constant BFG production is evident as well as the alternating production of BOFG that follows the converter batch operation. On the other hand, BOFG consumption by internal users is almost constant, while the BFG consumption by internal users has some variations between about 130 and 330 minutes with a peak between 130 and 230 minutes. POGs gasometers level dynamic, strictly linked with the control strategy, is showed in black lines in figures "b", together with minimum (cyan lines) and maximum (fuchsia lines) allowed levels. Figures 7c and 8c represent the real results of dynamic control simulations in terms of POGs distributed in syntheses reactors (purple) and PP (yellow) as well as of produced methane internally exploited for energy production (yellow) or externally sold (green).

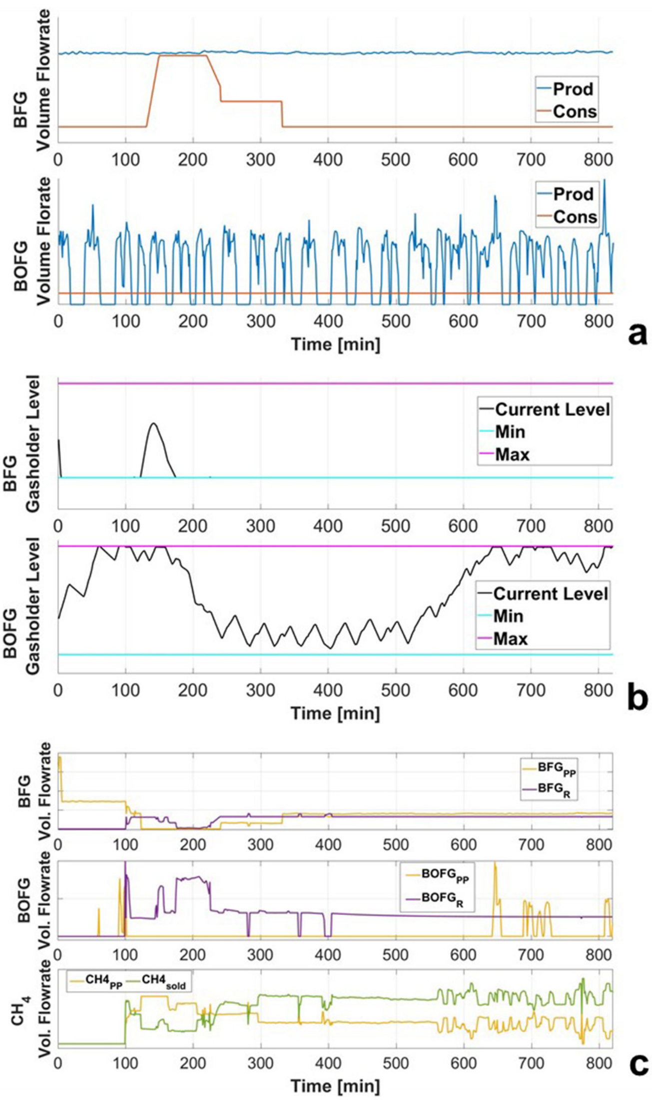


Fig. 7. Scenario 1 simulation results in case of green energy price of 5 €/MWh (y-axes values are not reported for confidentiality reasons): (a) POGs production and internal users consumption; (b) POGs gasholders level; (c) POGs distribution between PP (yellow) and syntheses reactors (purple) and CH_4 exploitation in PP (yellow) and external sold (green).

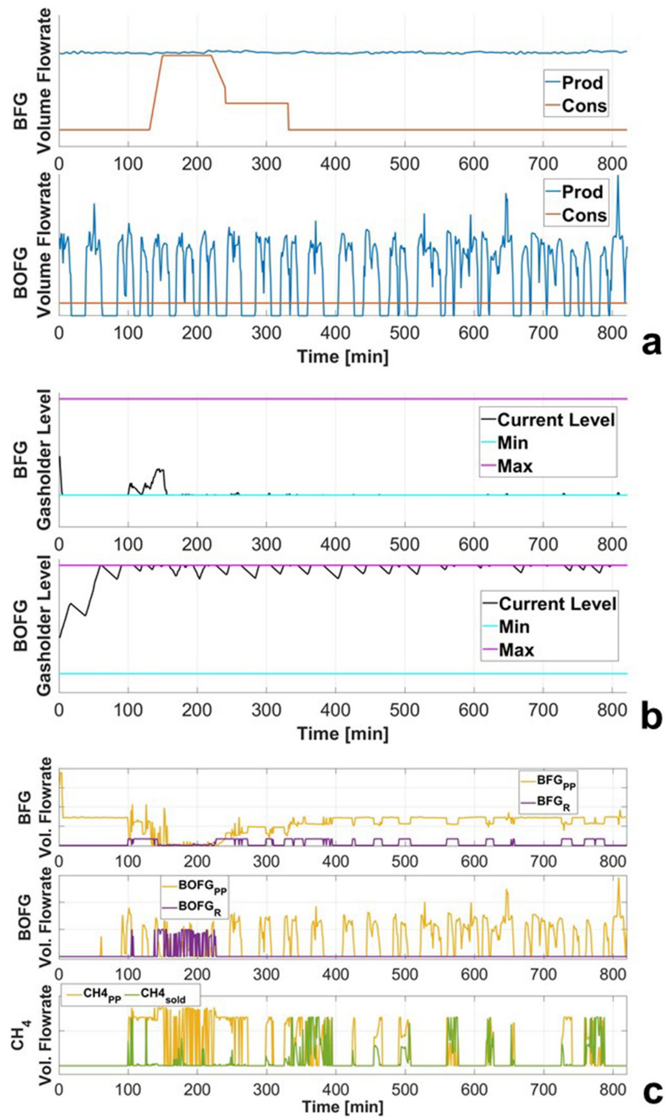


Fig. 8. Scenario 2 simulation results in case of green energy price of 18 €/MWh (y-axes values are not reported for confidentiality reasons): (a) POGs production and internal users consumption; (b) POGs gasholders level; (c) POGs distribution between PP (yellow) and syntheses reactors (purple) and CH_4 exploitation in PP (yellow) and external sold (green).

Starting from the analysis of Scenario 1 (i.e., the lowest green energy price scenario, whose results are depicted in Fig. 7), the simulation shows several interesting behaviors. The forecasted internal BFG consumption increase is translated in an attempt by the DC to anticipate the control action by reducing the BFG exploitation in the further users (i.e., PP and reactors) to increase the BFG availability in the gasholder to be used as soon as possible at the end of the disturbance (i.e., the consumption increase). During this disturbance period, BOFGs exploitation in the reactors is increased to continue a suitable methane production by avoiding reactions standby. Indeed, the continuous passages between standby and reaction modes are costs to be addressed and the DC tries to have an as stable as possible production, by avoiding several switches and aggressive control actions in the different control instants (high POGs inlet flowrates gradients are avoided). It is important to highlight that, to allow the use of POGs in the reactors, the DC manages also the PEM electrolyzer operation and, thus, the H_2 production: it tries to always have an excess of stored hydrogen and to minimize the costs related to the high green electricity consumptions. However, the most important result lies in the fact that with low green energy (and thus hydrogen) prices the DC sees the production of methane by H_2 enriched BFG and BOFG as a valid alternative to their use in PP. It aims at achieving both economic and environmental advantages, thanks to POGs

Table 4. Rough estimate of the amount of POGs and CH_4 required for the production of 1 MWh of energy and related amount of released CO_2.

Gas	NCV_g kWh/Nm^3	Amount Nm^3	Released CO_2 kg
BFG	1.0	1050	990
BOFG	2.4	409	576
COG	5.9	168	95
CH_4	10.5	96	187

valorization and reduction of CO_2 emissions (due to the reason discussed in the Introduction) and of primary raw material purchase (i.e., NG).

Different results were obtained in Scenario 2 related to a higher green energy price. Indeed, although the DC control actions are always characterized by "smooth steps" and by "prognostic behaviors", it does not continuously send POGs to the two reactors. In effect, it uses only one of them and exclusively for reducing the gasholders level: the reactors are in this case considered as "torches" to consume only surplus POGs that cannot be received by the PP. In this way, DC avoids waste of valuable resource and CO_2 emissions by circumventing the POGs flaring in torches, but does not consider the methane production economically viable in standard situations, due to excessive costs of hydrogen enrichment of POGs.

Concerning CO_2 reductions in the two analyzed scenarios, in both the cases CO_2 emitted if surplus of POGs is flared in torches is avoided; it can be computed from Scenario 2 where the syntheses reactors act as "torches" by using the POGs surplus. Through an estimate by considering this contribution, a reduction of about 420 t of CO_2 is obtained in the considered scenario period; it corresponds to a reduction of about 2.8% of emitted CO_2 [45]. Further reductions are obtained for the two reasons already explained in Section 1 and related to internal production of energy from lower amount of a higher energetic gas (i.e., CH_4) and to the avoidance of CO_2 emission related to the primary NG extraction and management. In this case, a dedicated analysis is required, that can be object of future work. However, Table 4 reports a rough estimate of the amount of POGs and CH_4 required for obtaining 1 MWh of energy (E_{ref}) and of the emitted CO_2 (CO_{2rel}), to provide first indications concerning the CO_2 emissions that can be avoided by exploiting produced methane in place of POGs for internal energetic/heating purposes. Gas NCV values (Tab. 4) and average compositions (Fig. 1) were considered in the computation as well as the chemical reactions of oxidation of CO and CH_4, reported below.

$$2CO + O_2 \rightarrow 2CO_2, \quad (15)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \quad (16)$$

The estimate of the amount of required gas (F_g) was obtained by exploiting the following equation (17); thermal efficiency of burners or of electrical generators was not considered in this simplified estimation.

$$F_g = E_{ref}/NCV_g. \quad (17)$$

The released CO_2 (CO_{2rel}) was calculated as the sum of CO_2 already contained in the considered gas (CO_{2g}) and the CO_2 generated (CO_{2gen}) with reactions (14) and (15), as follows:

$$CO_{2_{rel}} = CO_{2_g} + CO_{2_{gen}} \quad (18)$$

Only the use of COG leads to lower emission of CO_2 with respect to methane thanks to its high content of H_2 but in terms of amount, more COG is required. The other POGs releases significantly higher amount of CO_2 due to the higher amounts needed and their content of CO_2.

Accordingly, to the showed results, the cost of hydrogen production, through the required green energy, is the parameter affecting highly IS-POGs distribution for their different recovery and the consequent continuity of production of the syntheses reactors. This is more evident in Figure 9 that correlates the produced methane in the different scenarios carried out by varying the green energy prices. In the diagram, the methane production is normalized with respect to its production at lowest costs. The graph shows how increasing the renewable energy price reduces almost linearly the advantages obtained by producing methane from H_2 enriched steelworks POGs; CH_4 production is indeed increasingly avoided with the increase of renewable energy prices. In addition, a limit cost exists, after which the methane production is completely avoided by the DC because, despite the environmental advantages (i.e., reduction of CO_2 emission and of primary NG exploitation), it is not convenient from the economic point of view. It is important to highlight that the current green electricity price (i.e., about 50 €/MWh) is still too high to allow this POGs recovery route.

6 Conclusions, future expectations and possible transient strategies

The paper presents the evaluation of the hydrogen role in the exploitation of H_2-enriched IS-POGs for methane and methanol production. The investigation was carried out, firstly, through some preliminary stationary simulations that highlighted the significant amount of hydrogen required and allow considering PEM electrolyzers fed by green energy as the best hydrogen production process for the purpose. However, currently available hydrogen production sizes are not yet ready to allow obtaining the required H_2 amount for high scale production of CH_4 and CH_3OH from IS-POGs.

Afterwards, dynamic offline tests were described. They were realized by exploiting an ad-hoc developed DC including several dynamic models to simulate a real integration of this POGs usage in a real integrated steelworks. In these last scenarios, the green electricity price was varied to understand the behavior of the controller at its variation and the role of hydrogen

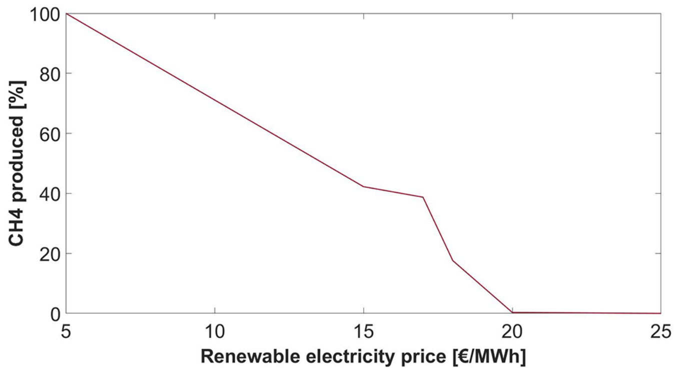


Fig. 9. Normalized methane production in function of renewable energy costs.

production that is highly dependent from the green energy availability and price. As expected, hydrogen produced by green electricity is the main parameter affecting the distribution of H_2-enriched IS-POGs for methane production and a green energy price of about 25 €/MWh is found to be the limit value to completely avoid this possibility.

Further investigations and more detailed economic and environmental analyses are ongoing or can be further refined, for instance by considering:

- further advantages linked with the hydrogen production by electrolyzers such as the production of significant amount of high purity oxygen to be internally exploited or externally sold;
- the convenience of the use of COG (i.e., source of H_2) after ad-hoc high efficiency cleaning treatments;
- the role of variation of CO_2 cost and the consequent change of found threshold for green energy price; it could be expected for instance that penalizing more the CO_2 emission, the H_2 price would be less impacting and more chemicals would be produced at higher green energy prices;
- the global amount of avoided CO_2, also the one related to the utilization of produced CH_4 against POGs or purchased NG for energy purposes (see Sects. 1 and 5).

However, the present study highlights how green hydrogen costs represent one of the main barrier for high scale valorization of IS-POGs in alternative material-based ways.

Therefore, future expectations are addressed not only to the development of highest capacity hydrogen production and storage technologies but especially to the creation of dedicated markets for an easy access to green hydrogen (or green electricity) by H_2-intensive industries/processes. The green hydrogen should become an intrinsic part of the European green energy system, by facilitation costs reduction.

In the meantime, R&D works are fundamental for improving the available technologies of hydrogen production or unconventional methane and methanol production from POGs as well as for evaluating transitory strategies to rapidly exploit and deploy the already available results/technologies. In this way, a step-wise achievement of the aimed target of decarbonization can be carried out by maximizing hydrogen use and gradually overcoming of all the existing barriers.

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